Alkali and Heat Treatment of Ti6Al4V and its Effect on Bioactivity

A THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF THE DEGREE OF

MASTER OF TECHNOLOGY

IN

BIOMEDICAL ENGINEERING

By

DIPANSHU BHARDWAJ

(Roll No. 212BM1350)

Under the guidance of

Dr. Amit Biswas

DEPARTMENT OF BIOTECHNOLOY & MEDICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

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CERTIFICATE

This is to certify that the thesis entitled, **"Alkali and heat treatment of Ti6AL4V and its effect on bioactivity"** submitted by **Dipanshu Bhardwaj** is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of requirements for the award of **Master of Technology in Biomedical Engineering at National Institute of Technology Rourkela**. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date: 25 May, 2014

Place: Rourkela

Superviser

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Date: 25 May, 2014 Dipanshu Bhardwaj

Place: Rourkela 212BM1350

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LIST OF ACRONYMS

Ti6Al4V: Titanium aluminum vanadium alloy

NaOH: Sodium hydroxide

Cp: Commercially pure

R: Rutile

A: Anatase

H: Hydroxyapatite

SME: Shape memory effect

NiTi: Nitinol

XRD: X-ray diffraction

Co-Cr: Cobalt Chromium

HA: Hydroxyapatite

10M, 700°C: 10 molar NaOH treatment and heat treatment at 700°C

ABSTRACT

Titanium and its alloys have wide applications in biomedical devices and components, specifically as hard tissue replacements and in cardiac and cardiovascular applications, because this material has comparatively low modulus, good fatigue strength, low density, high strength to weight ratio, formability, machinability, corrosion resistance, and biocompatibility.The present work has been carried out to study the formation of bone like apatite by alkali and heat treatment of Ti-6Al-4V alloy in the HANK solution. The study includes the formation of hydroxyapatite layer by changing the concentration of NaOH solution and heat treatment temperature. Different characterization techniques were used to study the chemical composition and surface morphology of the samples. XRD analysis was carried out to confirm the presence of hydroxyapatite layer. Vickers Hardness test was also carried out for all different samples. From the XRD analysis it was found that Ti-6Al-4V treated with 15 molar NaOH and subsequent heat treated at 600^{o} C shows the better formation of hydroxyapatite layer on the surface. It is evident from the result that the inducement ability of hydroxyapatite is maximum for alkali treated surface having 15 molar NaOH solutions.

Keywords: Titanium alloys, alkali treatment, heat treatment and hydroxyapatite

CHAPTER 1

INTRODUCTION

1 INTRODUCTION

The biomaterials are the materials of natural or synthetic origin, generally used to repair, replace and help to regenerate the damaged soft and hard tissues. The Clemso University Advisory Board for Biomaterials formally defines a biomaterial to be a systemically and pharmacologically inert material designed for implantation within or combination with living tissue". The basic criteria for satisfactory performance of a biomaterial implant in the body fluid are suitable chemical responses, mechanical properties and biocompatibility etc. in addition to surface properties. Biomaterials can be used for complete replacement of soft and hard tissues or as the supportive devices like pace maker, catheter etc. It can be categorized into four types, namely metallic, ceramic, polymer and composite [1].

The interaction between the bio-system and topography of the implant material plays an important role for a successful implantation. The implant should integrate with surrounding tissue by adhesion to appropriate cells rather than forming a fibrous tissue capsule or inducing chronic inflammation. Some of the main determinants of the biological response to a material are the surface properties. They may affect cell adhesion by influencing the ability of the surface to adsorb specific proteins and/or altering the conformation of the adsorbed proteins. Cell function, activation, spreading and movement are also affected by the surface properties of the material. Materials from which implant devices are made (e.g., metals and polymers) are often not manufactured with surface conditions conductive to optimal functionality (e.g., adhering biocompatible materials, cellular coatings or host tissue); they require some form of conditioning and/or pre-treatment that will physically enhance the surface to promote its adhesive properties to the desired tissue or coating material. Surface modification provides the ideal methods of altering the surface properties of the material through physical and mechanical process and/or by applying coating on the substrate [2].

Surface modification has several advantages over designing of highly corrosion resistant alloys and wear properties improvements. Desirable surface properties can be achieved while preserving the useful properties of the bulk material and therefore reducing the cost of the material. High corrosion and wear resistance, better biocompatibility, increased bone anchorage,

and improved aesthetic properties are among a few properties desired for suitable biomedical alloys and can be achieved through surface modification.

Now a days titanium and its alloys are being extensively used for the purpose of implantation, especially in hard tissue replacement for orthopedic and dental implant applications. Ti6Al4V is now being utilized as a common material for bone implants because of its high strength-to-weight ratio, low density, corrosion resistance, excellent biocompatibility, and good fatigue strength etc. Although possessing many suitable properties, Ti6Al4V alloy suffers from some limitations such as bio-inertness and inability to bond directly with living bone unlike the bioactive material such as bio-glass, hydroxyapatite and glass ceramics. It is observed that implanted titanium gets encapsulated by fibrous tissue that isolates them from the surrounding bones [3].

The techniques used for the improving the bone bonding capacity of the titanium-based implants surface are plasma spraying, sol-gel method, electrophoretic deposition, ion implantation etc. These techniques used bioactive materials such as hydroxyapatite, bio-glass as coating material to make bioactive surface of metallic implant materials. These coating techniques also required post sintering to increase the density of coating material and increase adhesion strength between substrate materials and coating material [4]. But the post sintering process carried out at very high temperature also leads to detrimental effects such as change in chemical composition and crystallinity of coating material which limits their applications. Chemical treatments such as alkaline treatment, H_2O_2 treatment are other popular techniques that can be used to modify the surface of metallic implant materials. These techniques enable the surface of implant material to induce apatite layer in living environment[5].

In this study alkaline treatment was utilised to modify the surface of Ti6Al4V alloy. This method is very simple and cost effective for modifying the surface of metallic implants. 10M, and 20M NaOH alkaline solution were used and subsequent heat treatment were done at 600°C, and 700°C. The apatite inducement ability of samples was investigated.

CHAPTER 2

REVIEW OF LITERATURE

2 REVIEW OF LITERATURE

2.1 Biomaterial

Materials expected to function in intimate contact with living tissue and used in medical application like for making the implant devices and surgical tools are called as biomaterials. Biomaterials include several metals, polymer, ceramics and composite which are used to reconstruct or replace the damaged tissue in a safe, economic, and physiologically acceptable manner [6]. The basic criterion for satisfactory performance of a biomaterial implant in the body fluid is appropriate chemical responses, mechanical properties and biocompatibility etc. The compatibility characteristics in the functioning of implant devices include mechanical properties (strength, stiffness and property) , appropriate optical property , sterilizability and appropriate density [7].

2.1.1 Metals

The metals which are having excellent thermal and electrical conductivity and mechanical property can be used as biomaterial. Metals always have free electrons so they can transfer thermal energy and electric charge easily. The mobile free electrons hold the positive metal ions together[8]. Metals have very strong bonding and their packing fraction is also high, that increase its specific gravity and melting point. Due to the non-directional metallic bonding, the position of metal ion cannot alter crystal structure that makes it a plastically deformable solid. Some metals are utilized as passive substitutes for hard tissue replacement, for example, total hip and knee joints, dental implants, spinal fixation devices, bone plates, vascular stents, catheter guide wire, cochlea implants and screws because of their excellent electrical conductivity, corrosion resistance and mechanical property [9].The most commonly used metals for hard tissue replacement are stainless steel, titanium and its alloys, cobalt based alloys.

2.1.1.1 Stainless steel

On the basis of crystal structure stainless steel may be classified into martensitic, ferritic, austenitic and duplex (austenitic-ferritic) stainless steel. The first stainless steel called as type 302 in modern classification which has more corrosion resistant as compare to the vanadium steel [10]. To improve the corrosion resistance of stainless steel, a small amount of Mo added, this alloy known as the 316 stainless steel. For better corrosion resistance to chloride solution the

carbon content of 316-stainless steel reduce from .08% to .03% became known as 316L stainless steel. The compositions of this alloy are 17-18% Cr, 12-14% Ni, 2-3% of Mo and .03% carbon. In 316L stainless steel "L" stands for "low carbon", which increases the corrosion resistance. It is a single phase austenitic stainless steel and one of the most popular implant materials. The elastic modulus of stainless steel is 200 GPa which much greater than the bone (20GPa) which results in stress shielding. Due to the stress shielding effect stainless steel is not suitable for the load bearing implants [11].

2.1.1.2 Co-Cr- alloys

Co-Cr alloys known to be highly corrosive resistant to chloride environment under stress. Co-Cr alloy is highly corrosive resistant due to the formation of oxide layer (Cr2O3) on the surface [12]. The elastic modulus of Co-Cr alloy is 230-260 GPa which is much more as compared to bone (20GPa).CoCrMo alloy has been used for many decades in dentistry and, relatively recently, in making artificial joints. The wrought CoNiCrMo alloy is relatively new, now used for making the stems of prostheses for heavily loaded joints such as the knee and hip.The chromium enhances corrosion resistance as well as solid solution strengthening of the alloy [13].

2.1.1.3 Ti and its alloys

Titanium is the fourth abundant metal on earth which is found in oxide form. Titanium has same strength as that of stainless steel but with about half of its weight. Due to the oxide layer formation on the titanium surface, it is highly corrosive resistance and possesses excellent biocompatibility with body environment which makes it suitable for implant applications [14]. There are four grades of unalloyed commercially pure (cp) titanium useful for surgical implant applications. In titanium alloy, aluminium tends to stabilize the alpha phase and vanadium tends to stabilize the beta phase. The modulus of elasticity of titanium is 80-100 GPa, which is comparable to the human bone, which minimize the stress shielding due to mismatching of the modulus of elasticity. Ti and its alloy are bio-inert and can't make direct chemical bond with surrounding tissue [15]. Therefore, before the implantation various methods are applied to coat a thin film of bioactive material on it. The main advantages of titanium alloys are high corrosive resistance, biocompatible material, low density and high strength to weight ratio.Surface roughness of titanium alloys have a significant effect on the bone apposition to the implant and on the bone implant interfacial pull out strength. In general, on the rougher surfaces there are

lower cell numbers, decreased rate of cellular proliferation, and increased matrix production compared to smooth surfaces. Bone formation appears to be strongly related to the presence of transforming growth factor β 1 in the bone matrix. The titanium–nickel alloys show unusual properties i.e., after it is deformed the material can snap back to its previous shape following heating of the material [16]. This phenomenon is called shape memory effect (SME). The equiatomic TiNi or NiTi alloy (Nitinol) exhibits an exceptional SME near room temperature: if it is plastically deformed below the transformation temperature, it reverts back to its original shape as the temperature is raised [17]. The SME can be generally related to diffusion less martensitic phase transformation which is also thermo elastic in nature, the thermo elasticity being attributed to the ordering in the parent and martensitic phases. Another unusual property is the super elasticity. The super elastic property is utilized in orthodontic arch wires since the conventional stainless steel wires are too stiff and harsh for the tooth. In addition, the shape memory effect can also be utilized. Some possible applications of shape memory alloys are orthodontic dental arch wire, intracranial aneurysm clip,vena cavafilter, contractile artificial muscles for an artificial heart, vascular stent, catheter guide wire, and orthopedic staple [18].

2.1.2 Ceramics

Ceramics are the compounds made up of two or more than two materials with interatomic bonding at very high temperature. Ceramics are widely used in the hard tissue replacement due to their properties which are similar to the bone. Ceramics materials like bio-ceramics and bio-glasses are biocompatible. Bio-ceramics is subset of biomaterial. The ceramic materials used are not the same as porcelain type ceramic materials. Bio-ceramics are nearly related to either the body's own materials, or extremely durable metal oxides [19].

Ceramics are used in medical implants material, bone implant, artificial teeth and bones relatively commonplace. Surgical cements are also used in it. Joint replacements are coated through bio-ceramics materials to reduce corrosion resistance and wear. Other uses of bio-ceramics are in pacemaker, kidney dialysis machines and respirators. Bio-ceramics materials are Oxide ceramic, Silica ceramics, Carbon fibres, Diamond-like carbon [20].

2.1.3 Polymer

Small molecules called monomers are linked together into chains to form Polymer. This is achieved by the chemical processes of condensation and addition. Biopolymers can be

categorized into two classes, Natural polymers and synthetic polymers, based on the source. Natural polymers are found in nature and can be easily extracted, for example silk, wool, cellulose, proteins. Synthetic polymers like polyvinyl, polyethylene, polystyrene can be easily manufactured and are mainly used in disposable to long-term implants. Generally polymeric materials are used in soft tissue replacements as biomedical application[21]. Polymeric biomaterials can be easily manufactured to produce various shapes like latex, fibers, film etc. Elasticity of polymers makes it possible to use polymers as implant material in case of cardiovascular tissue applications. In addition to many advantages like biocompatibility, elasticity, there are certain disadvantages associated with biopolymers such as, poor mechanical properties, leeching problems, high water absorption, and easy alteration in surface property due to surrounding biomolecules [22].

2.2 Chemical surface modifications

The behaviour of the adsorption and desorption of biomolecules or bond and production of different types of mammalian cells on polymeric materials depends on the surface characteristics such as wettability, hydrophobicity/ hydrophobicity ratio, bulk chemistry, surface charge and charge distribution, surface roughness, and rigidity. Hence, Surface modifications are required to enhance performance of biopolymers in a biological environment. While modifying surface properties, bulk properties are retained. There are many techniques used to chemically modify the implant surfaces [6]. These techniques convert inert surface into bioactive surface.

For hard tissue replacement, implants should have ability of direct bone bonding essentially. The most direct approach to induce direct bone bonding is to coat the bioactive material on the surface of implant. Calcium phosphates are known for their bioactivity and bone binding ability. Furlong and Osborn in 1985 and by Geesink in 1986 first reported clinical trials on femoral stems with HA coating. After that calcium phosphate coatings have been extensively investigated as bioactive coatings on bio-inert implant materials, mainly hydroxyapatite and carbonate-apatite. Hydroxyapatite coated implants because increased dissolution rate which enhances release of calcium and phosphate ions, inducing a facilitated precipitation of biological apatite onto implant surface. This shows usefulness of calcium phosphate coated implants in bone healing process and biological fixation. Many techniques such as, plasma spraying, sol–gel

coating, electrophoretic deposition, ion implantation, etc. have been employed for coating calcium phosphate onto metallic implants surfaces [23]. These techniques are described as follows:

2.2.1 Thermal oxidation of titanium alloy

Thermal oxidised Ti6Al4V sample have better corrosion protective ability and it depend on the nature and thickness of the surface oxide layer. In the thermal treatment we simply put the samples in furnace and then we increase the temperature of the furnace at a particular rate. After the thermal treatment, oxide layer form on the surface of the Ti6Al4V. The nature and the thickness of the oxide layer depend on the treated temperature and the time duration of the treatment. The layer formed using the heat treatment is highly stable, provides protection against the harmful effects of aggressive environments and is responsible for the higher corrosion resistance.Based onthe corrosion protective ability, the untreated and thermally oxidized samples can be ranked as follows: CP Ti (800 °C)>CP Ti (650 °C)>CP Ti (500 °C)>untreated CP Ti[24].

2.2.2 Acid treatment

Acid etching of titanium in HCl under inert atmosphere was examined as an alternative pretreatment to obtain a uniform initial titanium surface before alkali treatment[25]. Cp-Ti squares with an edge length of 10 mm and thickness of 1mm were washed in isopropanol and distilled water in an ultrasonic cleaner and subsequently dried at 100^0C. After the cleaning procedure the samples were etched in 37% HCl under inert atmosphere of argon at temperatures up to 50^0Cfor different times. The surface roughness increases with etching time and reaches a maximum of 4 mm during combined treatment at 50^0Cfor 90 min and 40^0C for 60 min. Atprolongedetchingtimeand elevated temperature the sample dimensions changed markedly which can in turn have a negative influence on the mechanical properties especially in the case of small or thin-walled implants. Contact angle measurements using sessile drop experiments reveals the hydrophobic behavior of the etched surface with contact angles of 115^0, whereas measurements on cp-Ti showed contact angles of 74^0C[26]

2.2.3 Alkali treatment

Alkali treatment facilitates the formation bioactive apatite layer on the surface of bioactive bioceramics, such as bioglass, hydroxyapatite and glass ceramic. This method is used to create bioactive Ti6Al4V implant with enhanced mechanical properties and excellent bioactivity. The Alkali and heat treatment can be described as follows; first the materials are immersed in a 5-20M NaOH or KOH solution for 24 h, and then washed with distilled water and ultrasonic cleaning for 5 min. The samples are then dried for 24 hr at 40^0C and finally heated to around 500–800°Cfor 1h. After the heat treatment, soaking of titanium in SBF for 4 weeks results in the bone like apatite formation on the surface, this indicates good bioactivity[27].

The reaction involved during alkali and heat treatment and apatite formation in SBF are described below[28]:

During the alkali treatment, the TiO_2 layer partially dissolves in the alkaline solution because of the attack by hydroxyl groups.

$$TiO_2 + NaOH \rightarrow HTiO_3^- + Na^+$$

This reaction is assumed to proceed simultaneously with hydration of titanium.

$$Ti + 3OH^- \rightarrow Ti(OH)_3 + 4e^-$$

$$Ti(OH)_3 + e^- \rightarrow TiO_2.H_2O + 1/2H_2\uparrow$$

$$Ti(OH)_3 + OH^- \rightarrow Ti(OH)_4$$

A further hydroxyl attack on the hydrated TiO2 produces negatively charged hydrates on the surface of the substrates as follows:

$$TiO_2.H_2O + OH^- \rightarrow HTiO_3^-.nH_2O$$

An alkaline titanate hydro gel layer is produced when these negatively charged species combine with the alkali ions in the aqueous solution. During heat treatment, the hydrogel layer is dehydrated to convert into crystalline alkali titanate layer. After immersion in SBF solution, Na^+ ions from the amorphous layer are exchanged by $H3O^+$ ions from the surrounding fluid resulting in Ti–OH layer, which is negatively charged and hence, combine selectively with the positively charged Ca^{2+}ions in the fluid to form calcium titanate. As the calcium ions accumulate on the surface, the surface gradually gains an overall positive charge[29]. As a result, the positively charged surface combines with negatively charged phosphate ions to form amorphous calcium

phosphate. The calcium phosphate spontaneously transforms into apatite because apatite is the stable phase in the body environment.

CHAPTER 3

OBJECTIVE OF PROJECT

3 OBJECTIVES

a) To prepare alkali titanate gel layer over Ti6Al4V surface by using different alkali concentrations (10M NaOH, 15M NaOH and 20M NaOH)

b) Heat treating the samples at various temperatures (500^0C, 600^0C and 700^0C) to obtain crystalline alkali titanate layer.

c) Preparation of hank solution using calcium chloride dehydrates, magnesium sulphate heptahydrate, potassium chloride, potassium phosphate dibasic anhydrous, disodium hydrogen phosphate dehydrates, sodium bicarbonate and Sodium chloride.

d) To study the hydroxyapatite inducement ability of the Ti6Al4V substrate after alkali and heat treatment.

e) Finally optimising the bioactivity of alkali and heat treated Ti6Al4V samples.

CHAPTER 4

MATERIALS AND METHOD

4 MATERIALS AND METHODS

4.1 Methodology

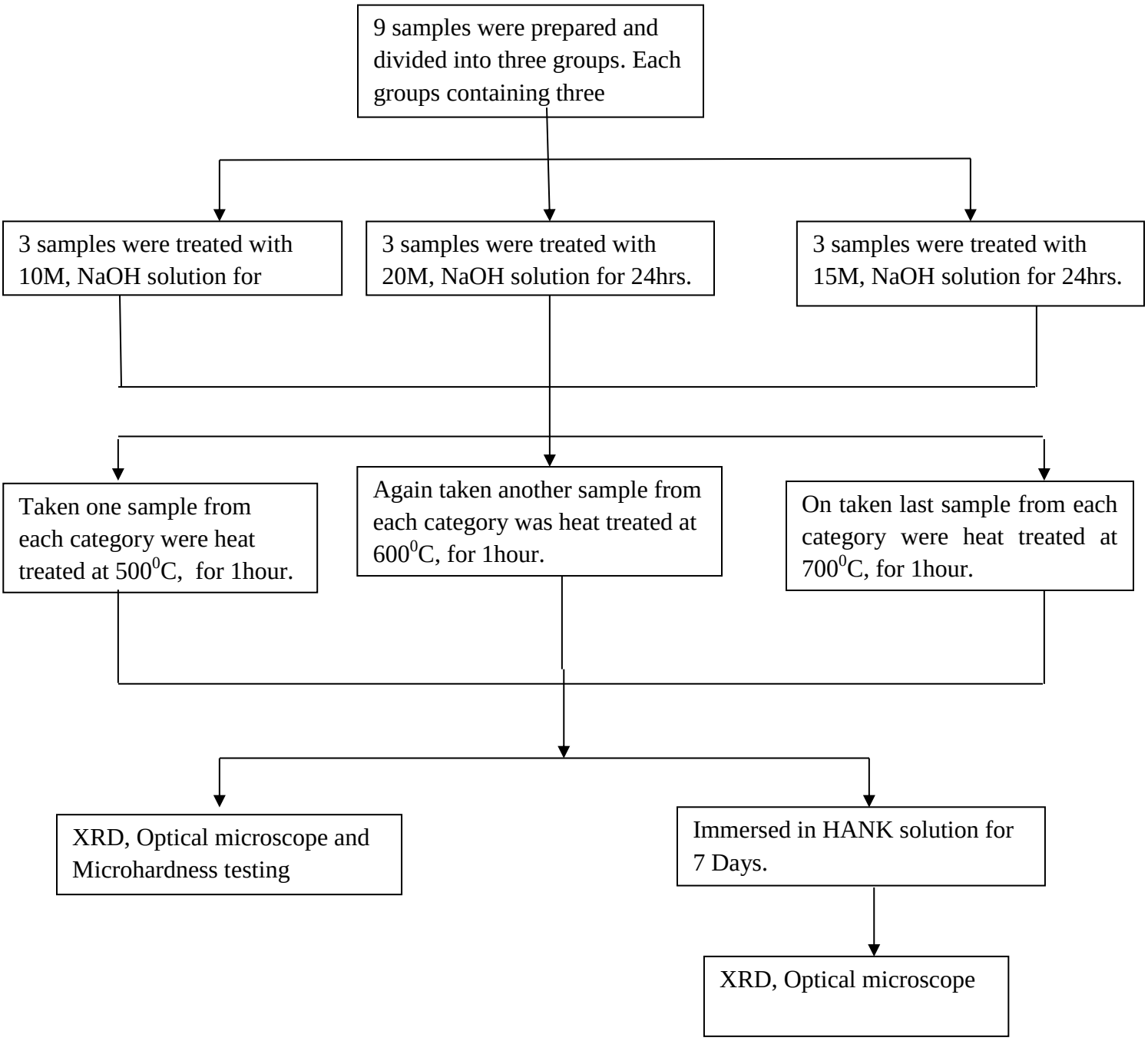

Figure 4.1: Flow chart of experimental procedure

4.2 Preparation of samples

4.2.1 Cutting

Ti6Al4V specimens of dimensions around 15mm×10mm×3mm were cut from titanium alloy sheet. Hand hacksaw was utilized as a slicing apparatus to cut the specimen.

4.2.2 Grinding

After cutting of samples grinding was done. For this study grinding was done on belt grinder to make smooth edges of samples.

4.2.3 Paper polishing

Specimens were polished utilizing three sorts of emery paper (1/0, 2/0, 3/0). These papers have grating particles on their surface. The roughness of emery papers diminish as moving from 1/0 to 3/0. Successful polishing was attained by utilizing two continuous emery papers as a part of the perpendicular meld on the Ti samples. Paper Polishing was mainly done to remove the particle roughness of the titanium samples.

4.2.4 Cloth polishing

Cloth polishing additionally called buffing was utilized for completing the polishing methodology. Cloth polishing was carried out after paper polishing. It was done using a nylon cushion on a material cleaning wheel. This cloth polishing was ruined evacuating the lines that stayed after paper cleaning.

4.2.5 Diamond polishing

Diamond polishing was carried out after cloth polishing. It was performed to eliminate light scratches that stayed after cloth polishing. In this procedure, diamond paste was used along with Hi-Fin spray. This was the last completing venture of polishing of the samples. At last, a mirror-like surface was obtained.

4.3 Alkali treatment

10M, 15M and 20M NaOH solution was made and three samples were dipped in each type of solution for 24 h, and then washed with distilled water for 5 min. After that the samples were dehydrated for 24 h at room temperature.

During the alkali treatment, the TiO_2 layer partially dissolves in the alkaline solution because of the attack by hydroxyl groups.

$$TiO_2 + NaOH \rightarrow HTiO_3^- + Na^+$$

This reaction is assumed to proceed simultaneously with hydration of titanium.

$$Ti + 3OH^- \rightarrow Ti(OH)_3 + 4e^-$$

$$Ti(OH)_3 + e^- \rightarrow TiO_2.H_2O + 1/2H_2\uparrow$$

$$Ti(OH)_3 + OH^- \rightarrow Ti(OH)_4$$

A further hydroxyl attack on the hydrated TiO_2 produces negatively charged hydrates on the surface of the substrates as follows:

$$TiO_2.H_2O + OH^- \rightarrow HTiO_3^-.nH_2O$$

An alkaline titanate hydro gel layer is produced when these negatively charged species combine with the alkali ions in the aqueous solution.

4.4 Heat treatment

The alkali treated samples were heat treated at different temperature (500°C, 600°C and 700°C) to convert the hydrogel layer into crystalline alkali titanate layer. The samples were heat treated in a furnace in the vicinity of air. Throughout the heat treatment, the temperature was progressively expanded from room temperature; about 15°C/minute to final temperature and hold final temperature for one hour and then samples were subjected to a furnace cooling.

4.5 Preparation of hank solution

The compositions of HANK solution were as followed:

Table 3: Chemical composition of hank solution

S.N.	INORGANIC SALTS	QUANTITY(mg/l)
1.	Calcium chloride dehydrate	187.400
2.	Magnesium sulphateheptahydrate	200.000
3.	Potassium chloride	400.000
4.	Potassium phosphate dibasic anhydrous	600.000
5.	Disodium hydrogen phosphate dehydrate	90.000
6.	Sodium bicarbonate	350.000
7.	Sodium chloride	8000.000

4.6 Immersion of samples into the hank solution

Nine samples (10M 500°C, 10M 600°C, 10M 700°C, 15M 500°C, 15M 600°C, 15M 700°C, 20M 500°C, 20M 600°C, 20M 700°C) were immerged in the hank solution for 5 days at room temperature.

4.7 Characterization of samples

The characterization of alkali and heat treated samples done by various characterization techniques. The phase analysis of the treated samples has done by X-ray diffraction technique. The morphology analysis of samples was done by optical microscope. The microhardness testing was done by LECO microhardness testing machine.

4.7.1 Phase analysis (XRD)

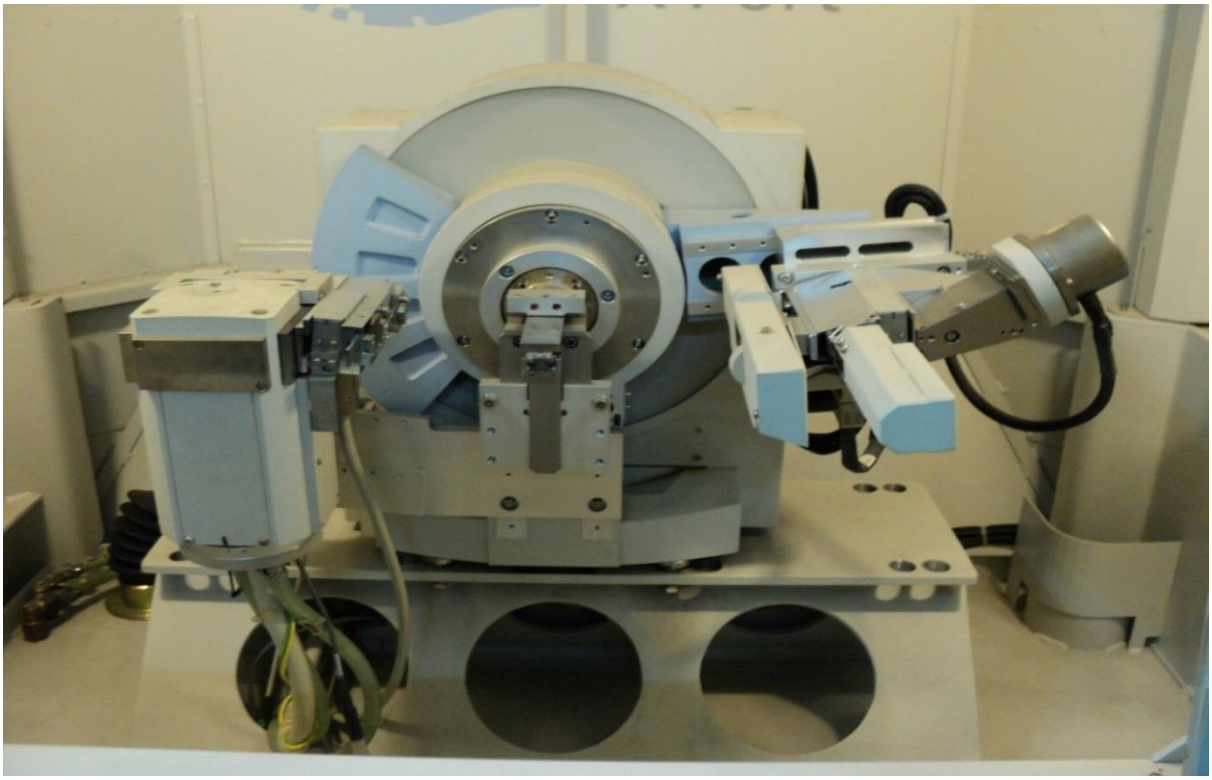

Figure 4.2: XRD Machine for phase characterization Model No. - X` Pert, 3040/00 Company- PAN Analytical

X-ray diffraction (XRD) is a powerful technique that extracts detailed information about the chemical composition and crystallographic structure of materials. The X-ray diffraction patterns of alkali and heat treated Ti6Al4V samples at various temperature were recorded on a Philips Analytical ltd, Holland (PW3040) using Ni-filtered CuKα radiation (λ = 1.5406A°) at 40 kV and 30 mA. The range for XRD characterization was selected as 30-80 degree with a scan speed of 3 degrees per minute.

4.7.2 Morphology analysis

Optical microscope from ZEISS with digital picture recording framework has been utilized for morphology analysis. The prepared sample was placed on the horizontal stage with the surface perpendicular to the optical axis of the microscope and illuminated through the objective lens

by light from a lamp or arc source. This light was focused by the condenser lens into a beam, approximately parallel to the optical axis of the microscope by a half-silvered mirror. The light then passed through the objective onto the specimen. It was then reflected from the surface of the specimen, back through the objective, the half-silvered mirror, and then to the eyepiece to the observer's eye, or to a camera port or a film plane. A comparative study of microstructures of the as received Ti6Al4V specimen as well as various electrochemically treated Ti6Al4V has been done in the next chapter.

Figure 4.3: Metallurgical binocular compound microscope equipped with digital image recording system.

4.7.3 Microhardness test

Microhardness of the alkali and heat treated sample and the samples after immersing in the hank solution were determined by using LECO microhardness testing machine. The machine was equipped with minimum 1gf and maximum 1000gf load. Initially before testing, the vertical lines seen through the eyepiece was calibrated. The vertical lines were adjusted such that their edges were adjacent to each other. The reset button was pressed and then the sample was placed on the horizontal platform for indentation. The test was carried out with 400 gf load with dwelling time 10 seconds to ensure that the indentation was up to the oxidized surface. For each sample, three different locations were indented and their hardness was recorded. These values were then averaged to get the overall hardness of the required samples.

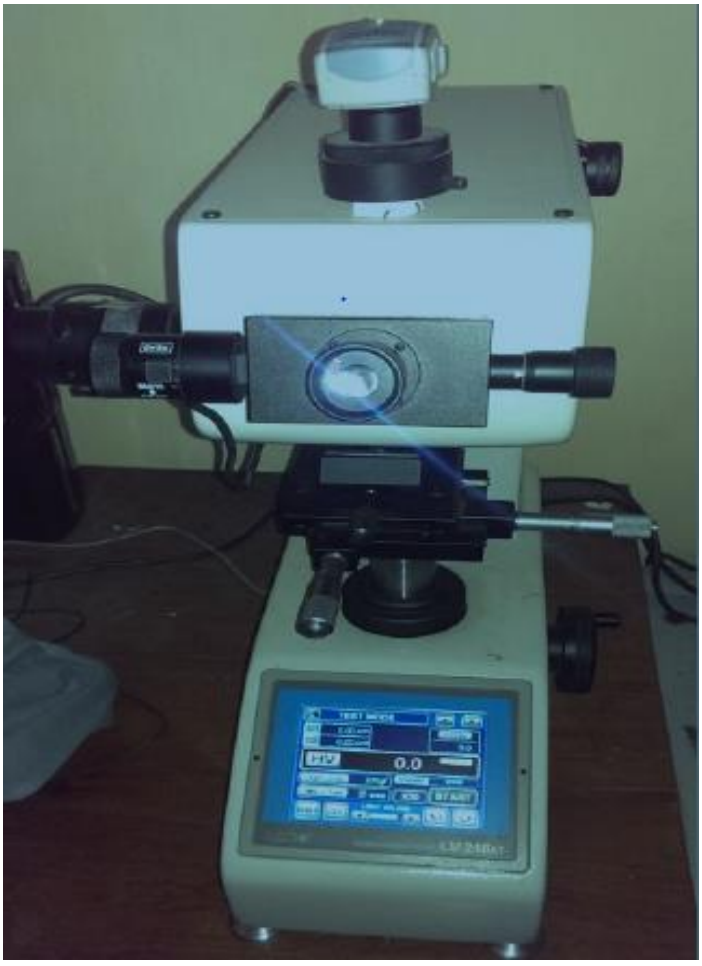

Figure 4.4: LECO Microhardness tester for measuring vickers hardness

CHAPTER 5

RESULT AND DISCUSSION

5 RESULTS AND DISCUSSION

Alkali and subsequent heat treated Ti6Al4V samples, at various alkaline concentrations (10M,15 M and 20M NaOH) and heat treatment temperatures (500°C, 600°C and 700°C) have been analysed before soaking and after soaking these samples in HANK solution for 5-days. Analysis of these samples is done on the basis of surface morphology with the help of optical microscope, possibility of various compounds on the surface of these samples has been identified with the help of X-ray diffraction (XRD) and the hardness of the alkali treated and heat treated sample were determined by using the LECO microhardness tester.

5.1. Morphology Analysiser

The influence of alkali and heat treatment, on the surface morphology of Ti6Al4V samples and Ti6Al4V samples soaked in the HANK solution was analyzed by optical microscope. Titania layer formed on the titanium decreased the bioactivity of titanium metal [27]. Alkali treatment of Ti6Al4V with NaOH solution led to the formation sodium titanate hydrogel layer on the surface On heat treatment this layer transformed into crystalline sodium titanate layer which enhances the apatite formation when kept in hank solution [28].

Figure 5.1 (a), (c) and (e), shows the optical micrographs of the alkali and heat treated Ti6Al4V sample at 10 M concentration. From Figure 5.1 (a) it was observed that an alkaline titanate layer was formed on the substrate treated at a temperature of 500°C. When the same treated sample was heat treated at a higher temperature i.e. at 600°C shown in Figure 5.1 (b) the crystalline nature of the sample was found to be increasing. At 700°C the alkaline titanate layer formed on the Ti6Al4V sample started peeling-off from the sample due to weak layer i.e. when temperature increases, the gel layer formed on the substrate was converted into crystalline phase enhancing the brittleness of the layer.

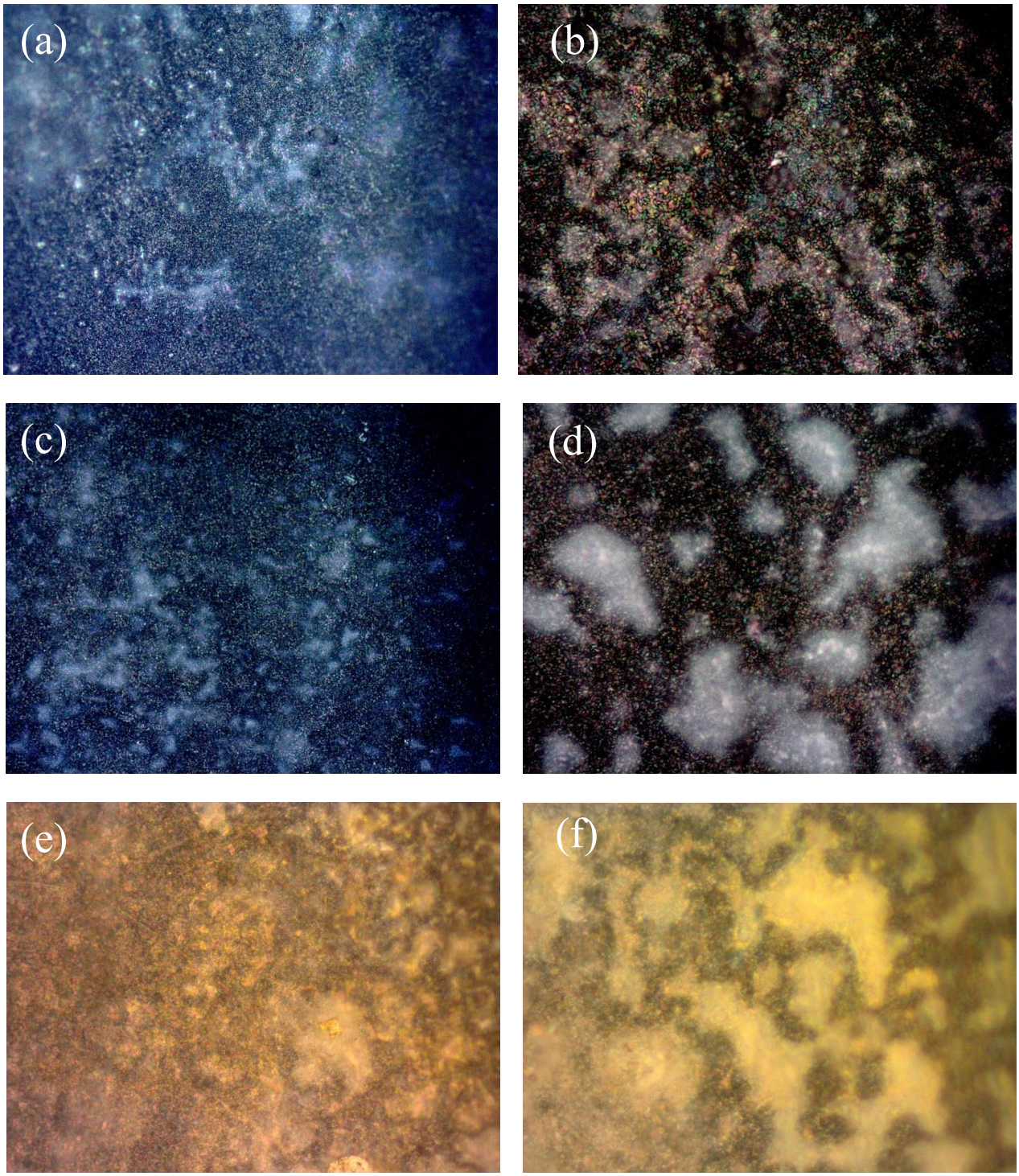

Figure 5.1: Optical Microscopic images of alkali treated Ti6Al4V in 10M NaOH solution after (a) Heat treated at 500°c, (b) Dipped in hank solution for 5 days for (a), (c) Heat treated at 600°c, (d) Dipped in hank solution for 5 days for (c), (e) Heat treat treated at 500°c, (f) Dipped in hank solution for 5 days for (e)

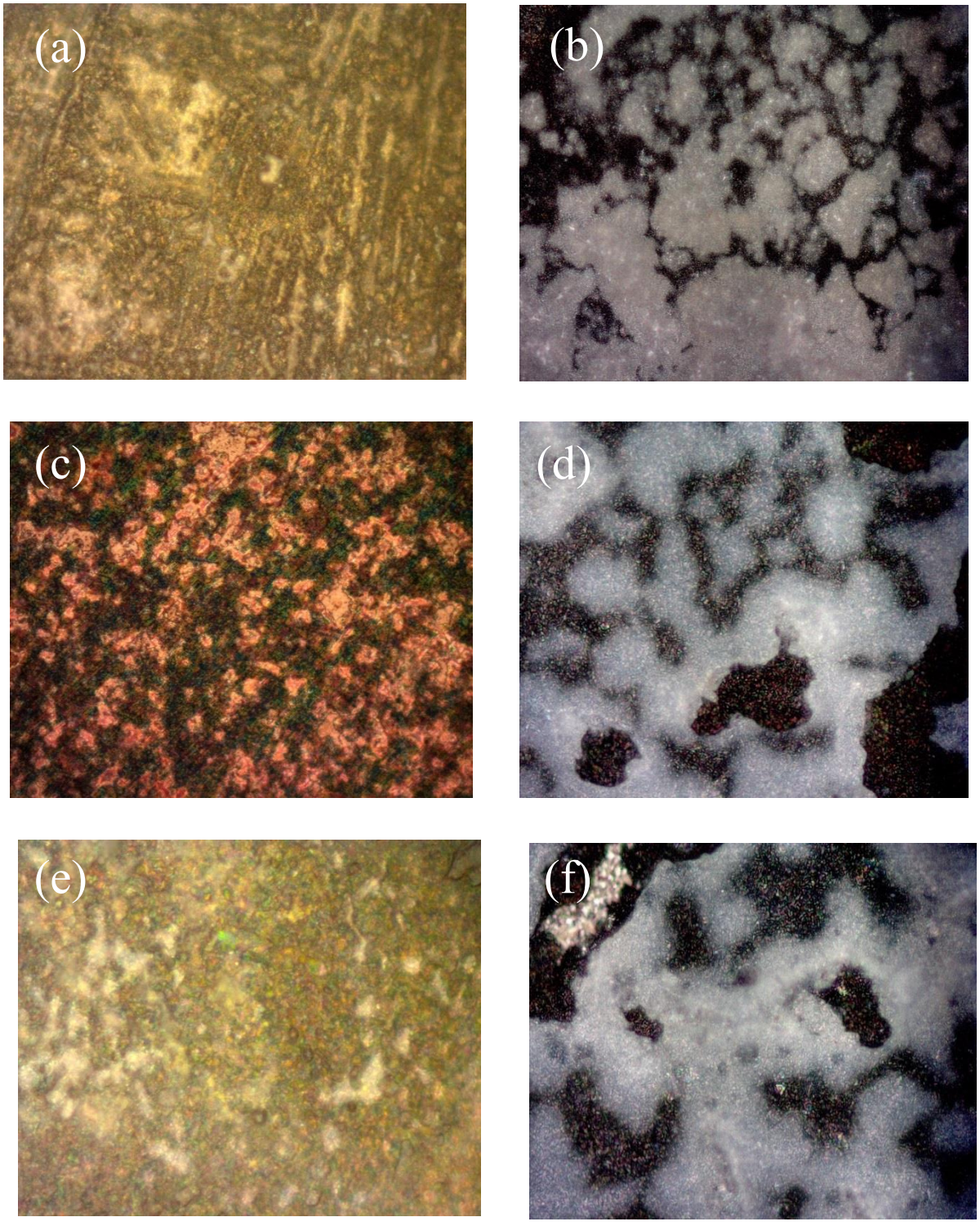

Figure 5.2: Optical Microscopic images of alkali treated Ti6Al4V in 15M NaOH solution after (a) Heat treated at 500°c, (b) Dipped in hanks solution for 5 days for (a), (c) Heat treated at 600°c, (d) Dipped in hanks solution for 5 days for (c), (e) Heat treated at 500°c, (f) Dipped in hank solution for 5 days for (e)

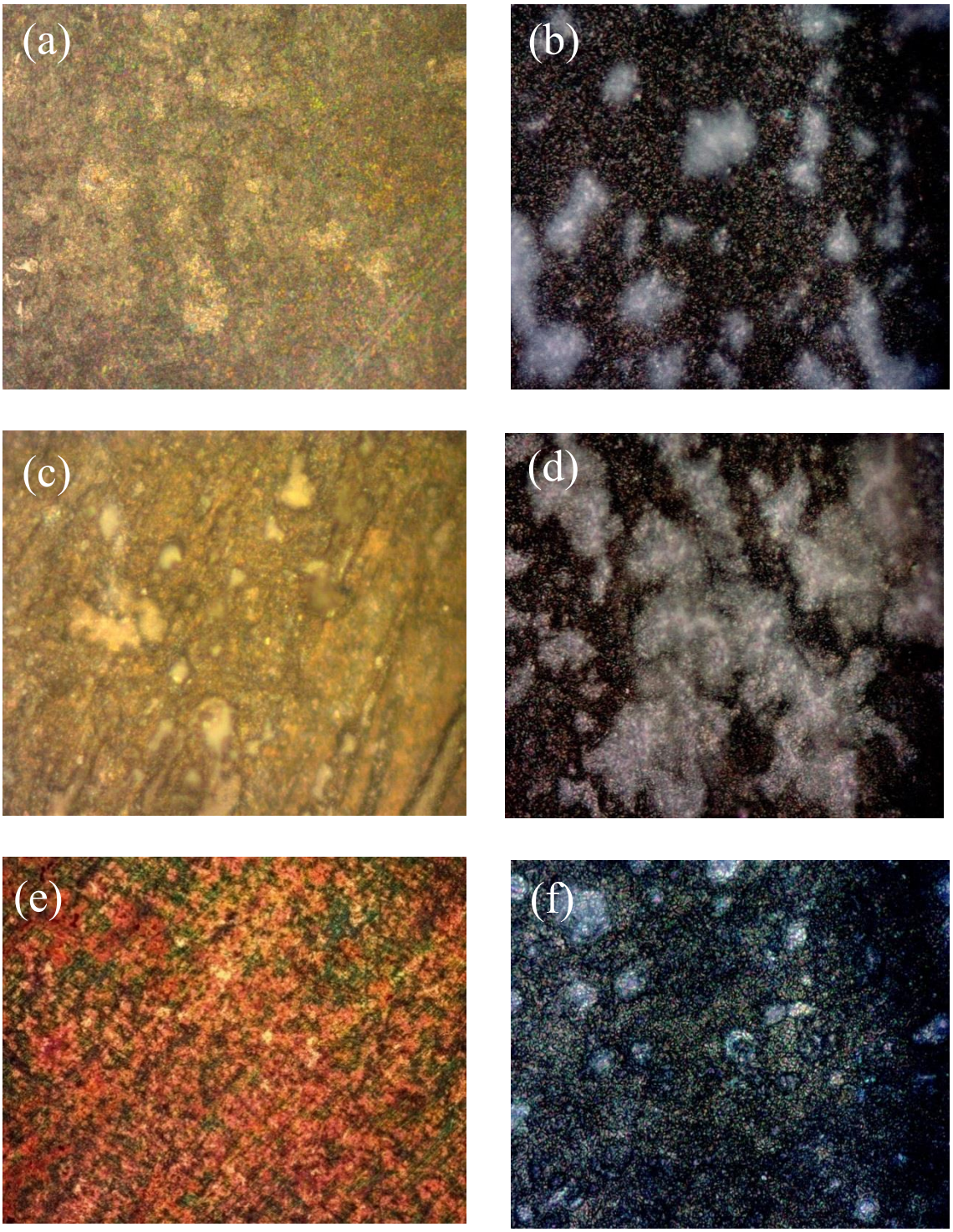

Figure 5.3: Optical Microscopic images of alkali treated Ti6Al4V in 20M NaOH solution after (a) Heat treated at 500°c, (b) Dipped in hanks solution for 5 days for (a), (c) Heat treated at 600°c, (d) Dipped in hanks solution for 5 days for (c), (e) Heat treated at 500°c, (f) Dipped in hank solution for 5 days for (e)

Figure 5.1 (b), (d) and (f) show the sample treated with hank solution. It was observed from these images that when temperature was increased from 500°C-600°C the apatite formation was also enhanced. As observed from the images the white clusters of apatite were formed. These clusters might be because of agglomeration of hydroxyapatite particles.
Finally the optical micrographs of titanium alloy was observed in 20M NaOH solution and noted that there are less cluster formation compared to that in 15M NaOH solution. Hence, the lesser cluster formation affected the thickness of the layer formed on the surface.

Figure 5.2 shows the optical micrographs of the titanium alloy treated with 15M NaOH solution. From these graphs thicker layer of titanate gel layer was observed which in turn increases the porosity of sample. For all the graphs in Figure 5.2 (a) to 5.2 (f) the results observed were found to be same with Figure 5.1 except its thicker apatite layer formation. The white clusters formation revealed the thicker layer on the surface.

From all the three NaOH concentrations (10M, 15M and 20M) investigated at 500°C, 600°C and 700°C, it was inferred that the maximum agglomeration occurs in a sample treated with 15M solution which was heat treated at 600°C. It was that the increase in temperature from 500°C-600°C, led to an increase in the apatite layer but with further increase in temperature ranging from 600°C- 700°C, the apatite layer gets thinner. At higher temperature around 700°C the maximum probable stable phase of titania is rutile. So due to decrease in amount of anatase at higher temperature the inducement of apatite formation get decreases. Anatase is more biocompatible than rutile. Whereas, the increase in concentration ranging from 10M-15M, leads to an increase in the apatite layer but with further increase in concentration ranging from 15M-20M, the apatite layer gets thinner.

5.2 Phase analysis (XRD)

The influence of alkali and heat treatment, on the crystalline structure of Ti6Al4V samples and the deposition of hydroxyapatite on the Ti6Al4V samples soaked in the HANK solution were observed by X-ray diffraction. It was performed to observe any phase change or presence of any impurity. The diffraction profile was taken from 30°-80° at scan rate of 3° per minute.

5.2.1 Phase analysis of alkali and heat treated samples before soaked in the HANK solution

Figure 5.4 (a) shows the XRD profile of Ti6Al4V alkali treated at 10M NaOH and heat treated at 500°C. The characteristics peaks of α titanium were observed at 40.4° and 71.2°. From XRD profile the presence of rutile and anatase phase was also observed. Rutile phase showed the peaks at 31.7° and 40.4° whereas anatase phase showed the peaks at 63.7° and 71.2°. No other phase or impurity was observed. Figure 5.4 (b) shows the XRD profile of Ti6Al4V alkali treated at 10M NaOH and heat treated at 600°C. Similar peaks were observed for titanium, rutile phase and anatase phase of titanium oxide. Intensity of the peaks was found to be increased by increasing the temperature upto 600°C. This increase in intensity and sharpness of peaks might be because of increase in crystallinity. Similar results were also found in literature [25].Figure 5.4 (c) shows the XRD profile of Ti6Al4V alkali treated at 10M NaOH and heat treated at 700°C. Characteristic peaks for titanium, rutile phase and anatase phase of titanium oxide were found. After further increasing the temperature upto 700°C it was found that more rutile peaks starts forming. On comparing all the XRD profiles in Figure 5.5 and Figure 5.6 with Figure 5.5, it can be concluded that the trend of formation of anatase and rutile phase is same irrespective of concentration of NaOH solution

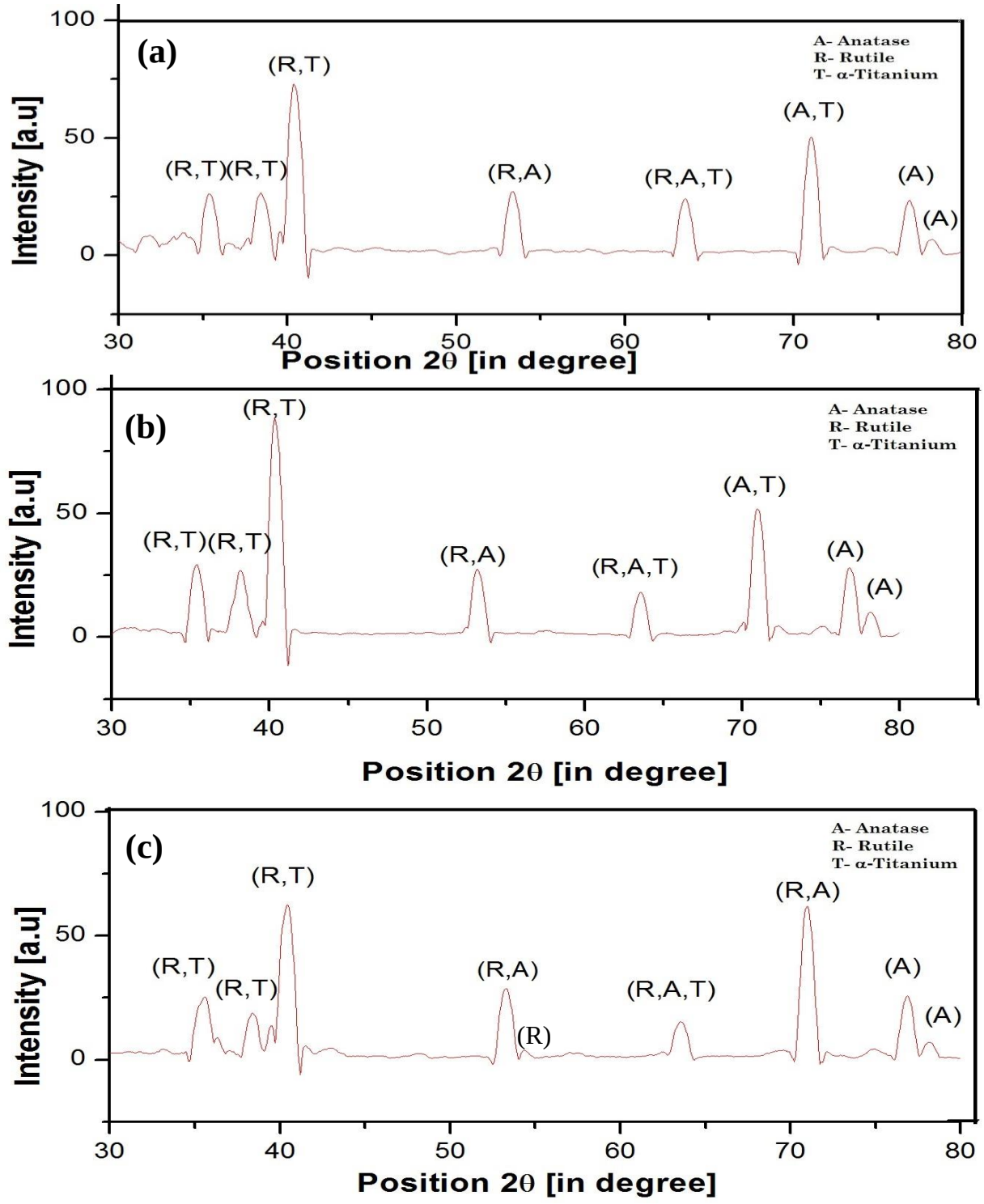

Figure.5.4: XRD pattern of Ti6Al4V alkali treated at 10M NaOH (a) Heat treated at 500°C, (b) Heat treated at 600°C, (c) Heat treated at 700°C.

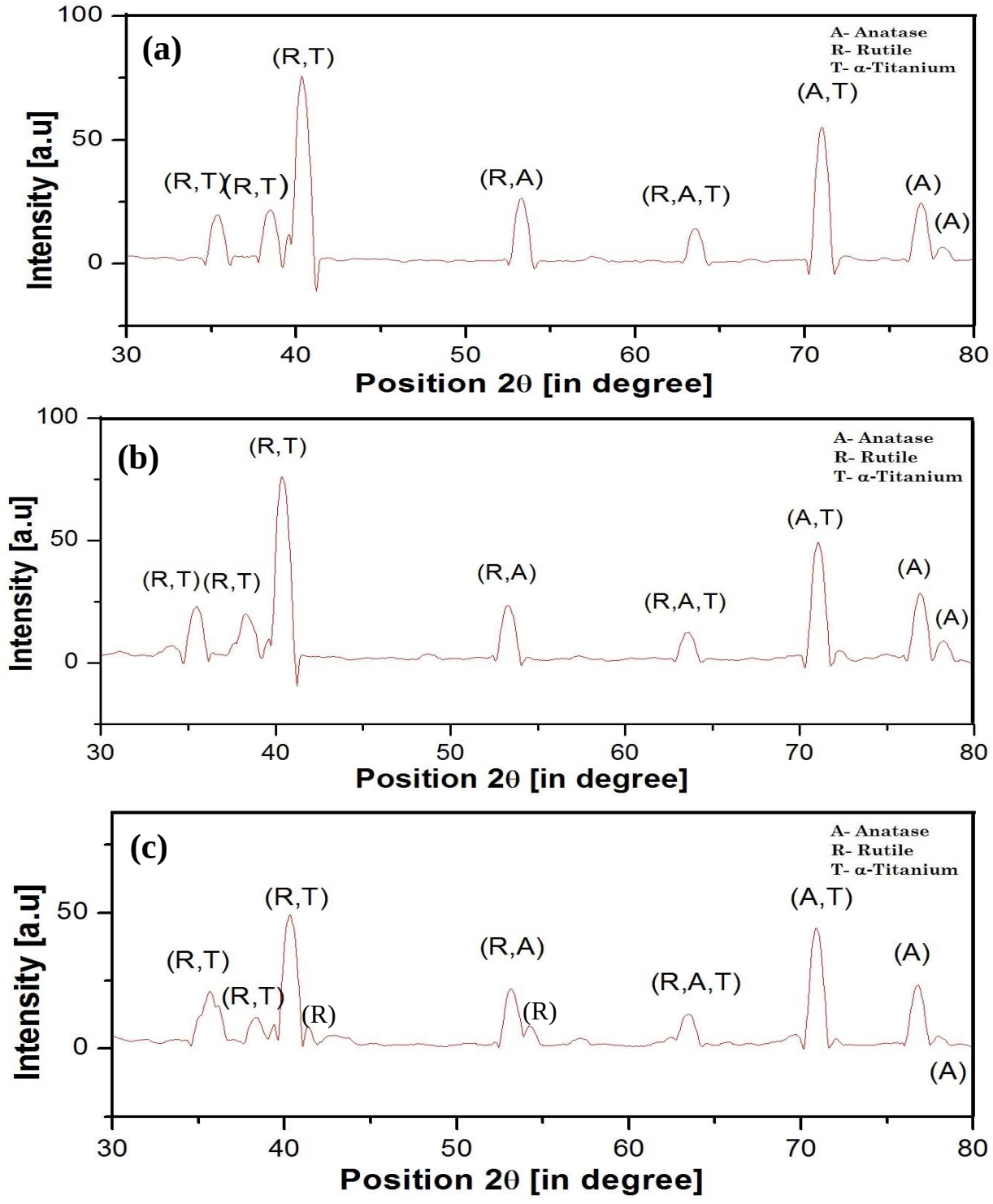

Figure.5.5: XRD pattern of Ti6Al4V alkali treated at 15M NaOH (a) Heat treated at 500°C, (b) Heat treated at 600°C, (c) Heat treated at700°C.

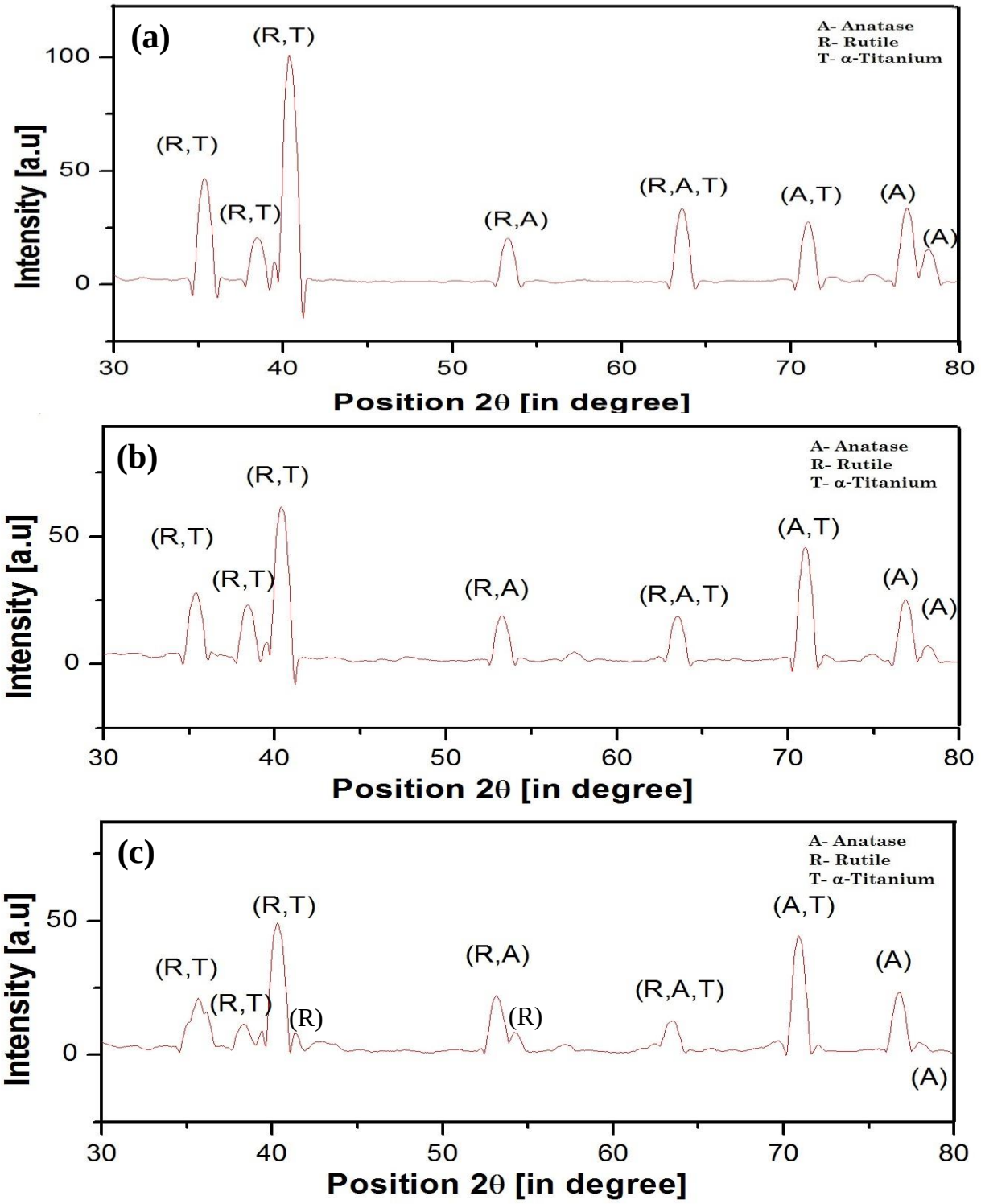

Figure.5.6: XRD pattern of Ti6Al4V alkali treated at 20M NaOH (a) Heat treated at 500°C, (b) Heat treated at 600°C, (c) Heat treated at700°C.

5.2.2 Phase analysis of alkali heat treated samples after soaked in the HANK solution

Figure 5.7 , 5.8 and 5.9 shows XRD pattern of Ti6Al4V alkali treated at 10M, 15M and 20M NaOH dipped in hank solution for 5 days (a) Heat treated at 500°C, (b) Heat treated at 600°C, (c) Heat treated at700°C. In these samples diffraction peaks for apatite formed were shown. Characteristic peaks of hydroxyapatite were observed at 32°, 45° and 54°. At 500°C lowest peaks were found for hydroxyapatite. With increase in NaOH molarity apatite formation was increased and was found to be maximum in terms of intensity for 15M NaOH. Heat treatment temperature also influence the inducement of hydroxyapatite on the surface of the titania and it was found that it show maximum at 600°C and this is possible due to more anatase formed at that temperature as can be seen from the Figure 5.4, 5.5 and 5.6.

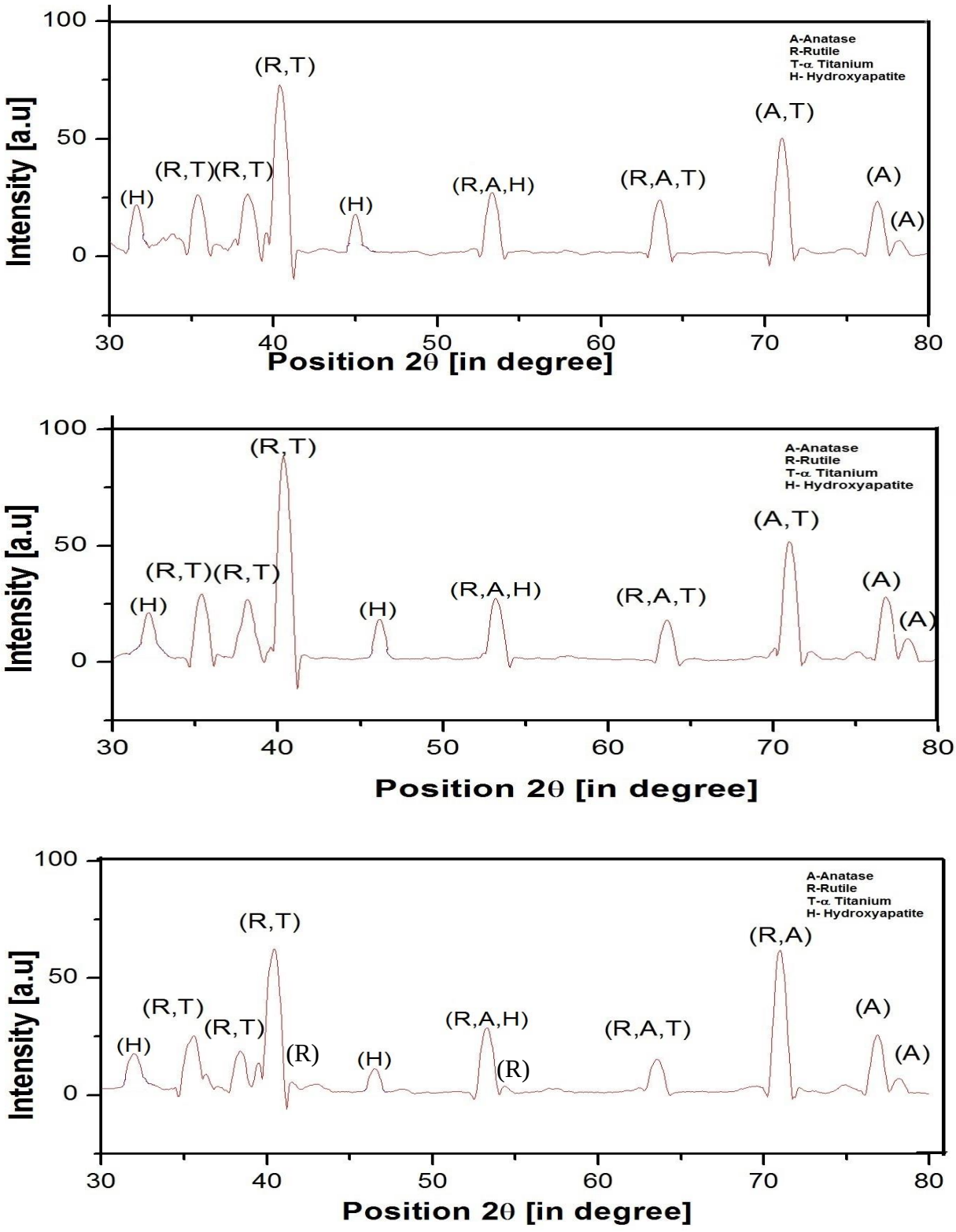

Figure 5.7: XRD pattern of Ti6Al4V alkali treated at 10M NaOH dipped in hank solution for 5 days (a) Heat treated at 500°C, (b) Heat treated at 600°C, (c) Heat treated at700°C.

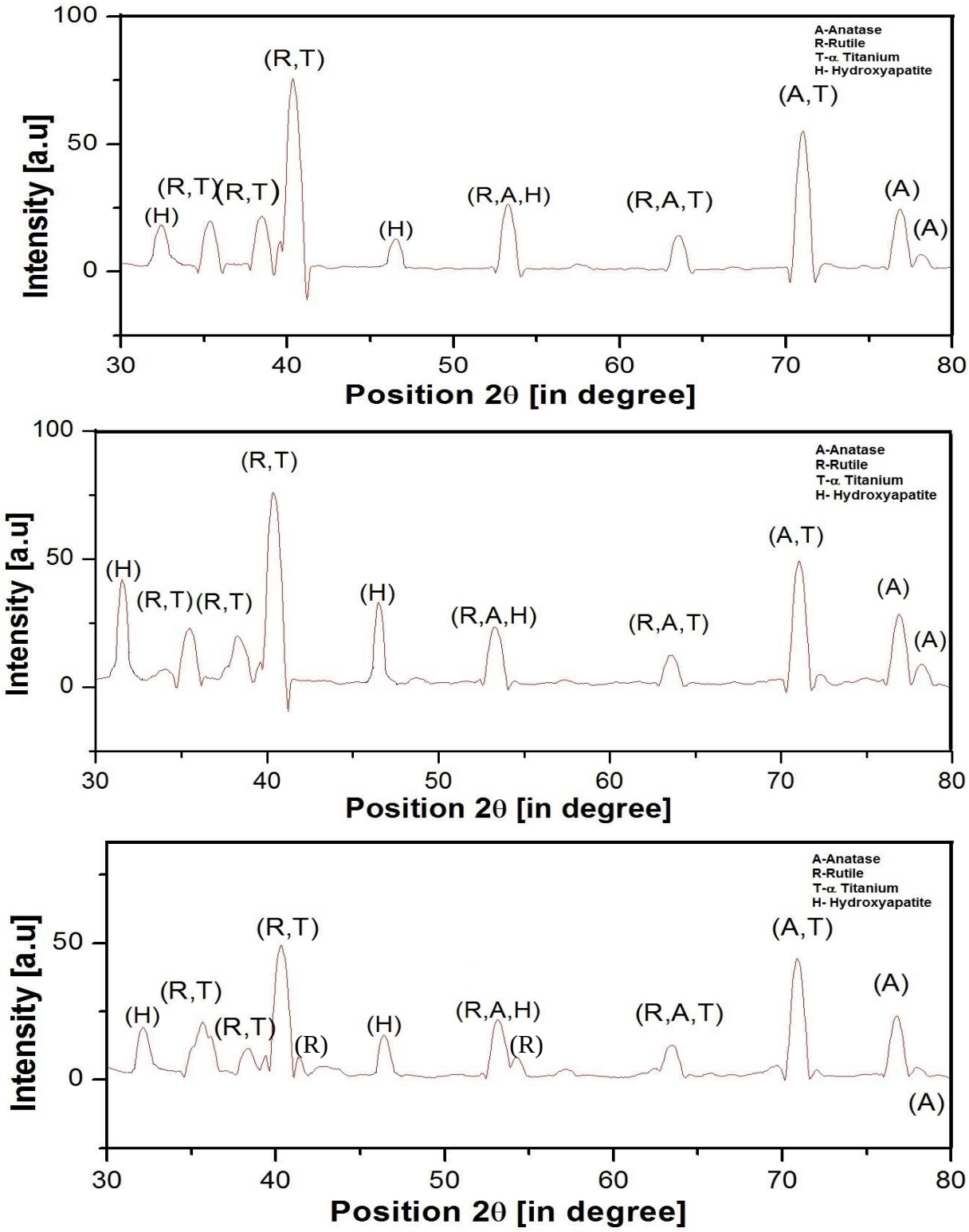

Figure 5.8: XRD pattern of Ti6Al4V alkali treated at 15M NaOH dipped in hank solution for 5 days (a) Heat treated at 500°C, (b) Heat treated at 600°C, (c) Heat treated at700°C.

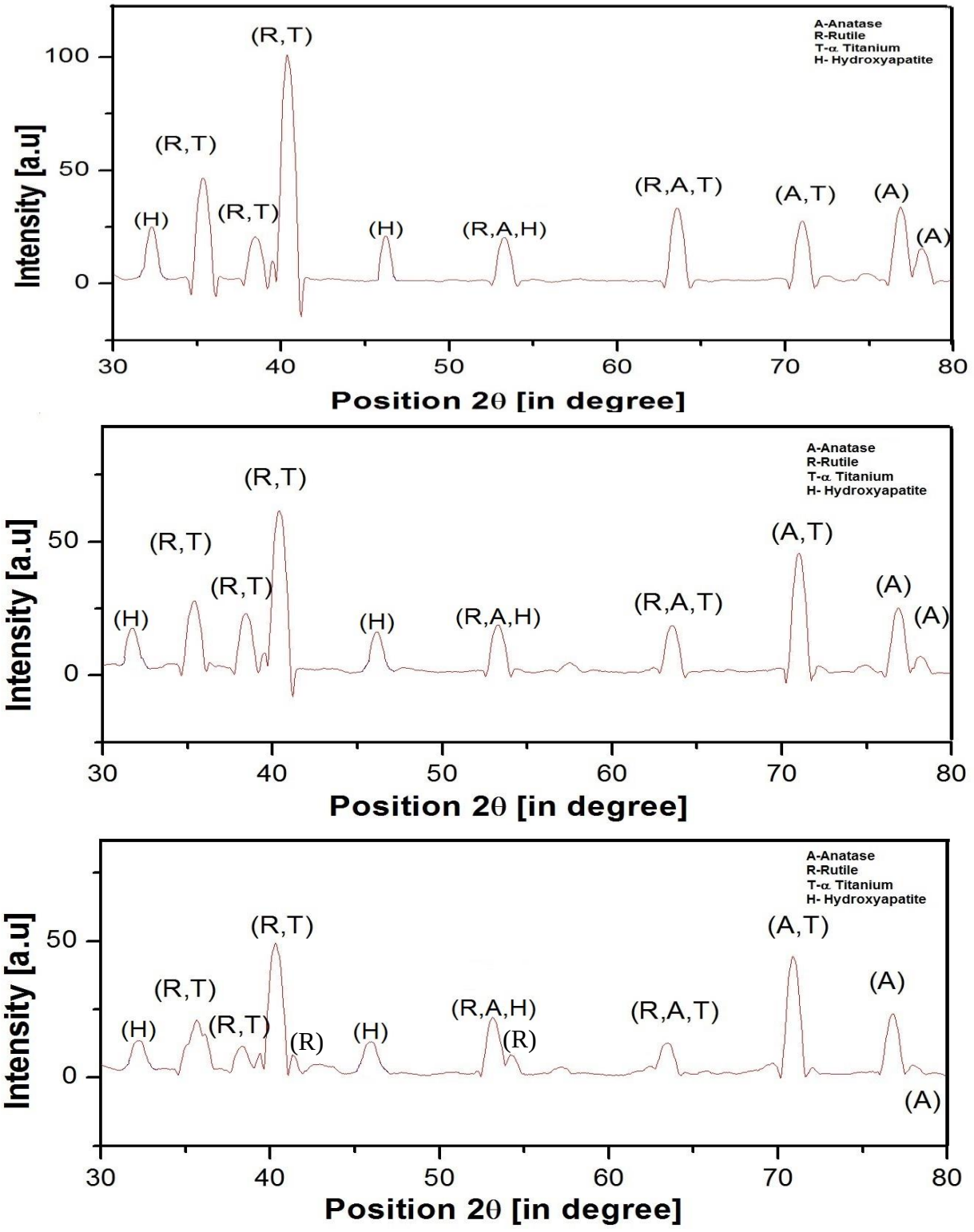

Figure 5.9: XRD pattern of Ti6Al4V alkali treated at 20M NaOH dipped in hank solution for 5 days (a) Heat treated at 500°C, (b) Heat treated at 600°C, (c) Heat treated at700°C.

5.3 Micro hardness Analysis

The microhardness of the various alkali and heat treated samples was evaluated using a vickers microhardness tester. All the tests were carried out at a load of 300 gf with indentation time 10 seconds. Table 2 shows the vickers hardness values of the Ti6Al4V sample which were alkali treated at various concentrations and temperature. The hardness was measured at five different locations and the average of them are taken for analysis.

The microhardness of the alkali and heat treated sample increased from the untreated samples. Heat treatment at higher temperature, increased the hardness compared to low temperature irrespective of the concentration of the alkali treatment. The concentration of the alkali has little affected on the hardness of the sample. The increase in hardness at high temperature was mainly attributed to the increase of rutile phase at high temperature.

Table 4: Microhardness of alkali and heat treated Ti6Al4V before and after dipped in hank solution for 5 days

Samples	**HV (gf/μm^2)**
Ti6Al4V untreated sample	310
10M alkali treated & heat treated at 500°C sample	325
10M alkali treated & heat treated at 600°C sample	390
10M alkali treated & heat treated at 700°C sample	525
15M alkali treated & heat treated at 500°C sample	350
15M alkali treated & heat treated at 600°C sample	490
15M alkali treated & heat treated at 700°C sample	550
20M alkali treated & heat treated at 500°C sample	380
20M alkali treated & heat treated at 600°C sample	555
20M alkali treated & heat treated at 700°C sample	590

CONCLUSION

The alkali treated samples were studied using XRD and optical microscope. The variations of different concentrations of NaOH solution along with temperature affects revealed the characteristic features of the Ti6Al4V. Notifiable inducement of hydroxyapatite was observed in the samples which were immersed into HANK solution.

The study of temperature effects on the samples done by incrementing it from 500°C to 600°C were found to significantly increase the inducement of hydroxyapatite layer. However, further increments of temperature ranging from 600°C to 700°C tend to diminution of the hydroxyapatite layer. Similarly, the concentration effects on Ti6Al4V also revealed the same characteristics exhibited by temperature effects. With increment in concentration from 10M to 15M, inducement of hydroxyapatite was observed to be increased. With the further increment this layer reduced significantly.

Among all the concentrations studied the sample treated with 15M NaOH solution for 24 hour and subsequent heat treatment at 600°C was found to exhibit the best inducement ability with a thick hydroxyapatite layer formation on the sample after immersion in HANK solution. In case of sample treated with 20M and 10M, NaOH solution and heat treatment at 700°C and 500°C for 24 hours revealed least inducement ability. Ti6Al4V sample treated with NaOH solution for 24 hour and subsequent heat treatment increased the microhardness of the surface which would improve wear property of the titanium alloy.

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